A Simple, Efficient, and Recyclable Phosphine-Free Catalytic System for Carbonylative Suzuki Coupling Reaction of Aryl and Heteroaryl Iodides

Ziyauddin S. Qureshi, Krishna M. Deshmukh, Pawan J. Tambade, Bhalchandra M. Bhanage*

Department of Chemistry, Institute of Chemical Technology (Autonomous), N. Parekh Marg, Matunga, Mumbai 400 019, India
Fax +91(22)24145614; E-mail: bhalchandra_bhanage@yahoo.com; E-mail: bm.bhanage@ictmumbai.edu.in

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Abstract: The carbonylative Suzuki cross-coupling reaction of arylboronic acid with aryl and heteroaryl iodides using polymer supported palladium–N-heterocyclic carbene complex (PS-Pd-NHC) as an efficient heterogeneous, recyclable catalyst is described. The developed catalytic system is found to be effective for the carbonylative coupling reaction of aryl, heteroaryl, and bicyclic heteroaryl iodides (5-iodoindole and 3-iodoquinoline) with various arylboronic acid derivatives providing good to excellent yields of the desired products. The protocol is advantageous due to the ease in handling of the catalyst and simple workup procedure, and environmentally benign with effective catalyst recyclability.

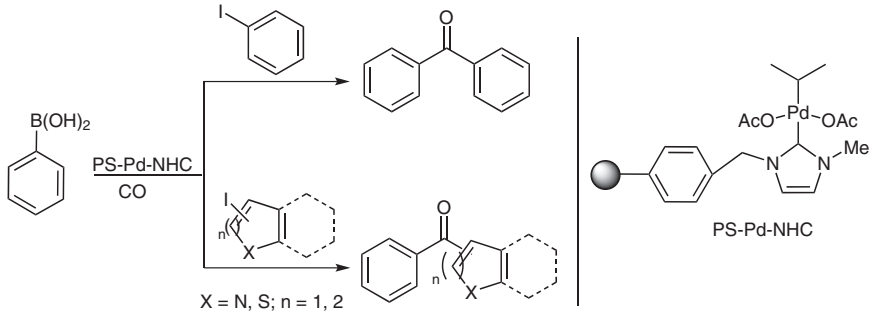
Key words: biaryl ketones, boron, heterogeneous catalysis, palladium, Suzuki carbonylation

Biaryl ketones are important building blocks in the synthesis of several natural products and pharmaceutical compounds.[1] They are usually prepared by Friedel–Crafts acylation of substituted aromatic compounds.[2] The major disadvantage of traditional Friedel–Crafts acylation is the use of excessive amount of Lewis acid and limiting regioselectivity towards *para*-position. Other described methods for the synthesis of biaryl ketones involves transition-metal-mediated, three component cross-coupling reaction between arylmetal reagents, carbon monoxide, and aryl electrophiles.[3–9] These carbonylative reactions have limitation due to the formation of biaryl side products without carbon monoxide insertion particularly with electron-deficient aryl halides.[10]

Recently, N-heterocyclic carbene (NHC) has gained considerable attention as an effective ligand for transition metals in homogeneous catalysis,[11] because of their effective binding ability to transition metals irrespective of their oxidation states. N-Heterocyclic carbene ligands reveal a very high dissociation energy as compared to phosphine ligand, which have been quantified via theoretical calculation for different metals.[12] Therefore, the binding between the NHC and transition metal is much stronger, and chemically and thermally more inert towards cleavage than that of other complexes. The NHC ligands can be bound to the polymer and explored for catalysis; as such polymer-supported catalysts offers various advantages such as reuse of expensive transition metals and ligands with a possibility to prevent the contamination of ligand residue in products. Various groups have studied the application of polymer supported palladium–NHC complex as a catalyst for Suzuki coupling reactions.[13]

In continuation of our interest on phosphine-free carbonylation reactions,[14] herein we report an facile protocol for the carbonylative Suzuki coupling reaction of arylboronic acid with aryl and heteroaryl iodides using polymer-supported palladium–NHC complex (PS-Pd-NHC) as a heterogeneous and recyclable catalyst for the first time (Scheme 1).

Initially, carbonylative Suzuki coupling reaction of iodobenzene with phenylboronic acid in the presence of (PS-Pd-NHC) complex was chosen as a model reaction, and the influence of various reaction parameters such as solvent, base, temperature, pressure, catalyst loading, and reaction time was investigated. It was observed that the nature of solvent affects the selectivity of the reaction. The reaction was found to work efficiently in nonpolar solvents as compared to the polar solvents. In polar apro-



Scheme 1 Carbonylative Suzuki coupling reaction of arylboronic acid with aryl and hetroaryl iodides

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tic solvents such as 1,4-dioxane (34%), THF (42%), and DMF (50%) low yield of the product was observed. Nonpolar solvents like toluene (94%) and diisopropyl ether (85%) were found to be highly effective providing excellent yield of carbonylated product. However, in the case of anisole, 40% yield of the desired product was observed. A polar protic solvent such as water was also found to give good yield (70%) of benzophenone. Further, we studied the effect of various bases like K_3PO_4, Cs_2CO_3, and Et_3N on reaction outcome, wherein K_2CO_3 was found to the best base giving an excellent yield of 94% for the expected product. It was also observed that the reaction did not proceed in the absence of base. In the case of temperature study, with decrease in the reaction temperature from 100 to 80 °C, decrease in the yield (65%) of desired product was observed. The other reaction parameters like influence of CO pressure, catalyst loading, and reaction time were also studied, and the optimum reaction conditions for carbonylative Suzuki coupling reaction of iodobenzene with phenylboronic acid were found to be PS-Pd-NHC (50 mg, 14.5 μmol), toluene as solvent, K_2CO_3 as base, and 100 psi of CO pressure, at 100 °C for 10 hours.

These optimized reaction conditions were then used for cabonylative Suzuki cross-coupling reaction of various aryl iodides with different arylboronic acids providing good to excellent yields of the desired products (Table 1, entries 1–15). Various electron-donating and electron-withdrawing groups such as Me, OMe, NH_2, COMe, NO_2, and Br on both aryl iodide and arylboronic acid smoothly underwent carbonylative Suzuki coupling reaction giving desired products with appreciable yields.

Iodobenzene reacts smoothly with phenylboronic acid giving 94% yield of benzophenone (Table 1, entry 1). The carbonylative cross coupling reaction of sterically hindered 2-iodotoluene and 2-iodoanisole with phenylboronic acid gives good yield (88–90%) of the respective products (Table 1, entries 2, 3). The reaction of 4-iodotoluene and 4-iodoanisole proceeded smoothly with slightly higher yields of corresponding carbonylated products (Table 1, entries 4, 5). The reaction of electron-rich 2-iodoaniline with phenylboronic acid yields 2-aminobenzophenone in excellent amount (93%, Table 1, entry 6). The reaction of aryl iodide bearing strong electron-withdrawing groups such as COMe and NO_2 also permits the carbonylative coupling reaction with phenylboronic acid giving 4-acetylbenzophenone (95%) and 4-nitrobenzophenone (91%) in excellent yields respectively (Table 1, entries 7, 8). The carbonylation of bulky 1-iodonaphthalene with phenylboronic acid offers 89% of benzoylnaphthalene (Table 1, entry 9). Interestingly 1,2-diiodobenzene under optimized reaction conditions provides selective monocarbonylated product (2-iodobenzophenone) with phenylboronic acid in moderate yield (Table 1, entry 10).

The effect of substituents on the phenylboronic acid was then investigated, and it was observed that both electron-donating and electron-withdrawing groups were well tolerated under present reaction conditions. Electron-donating groups like Me and OMe at *ortho*- and *para*-position of boronic acid provides good to excellent yield of the corresponding ketones (Table 1, entries 11–14). The present catalytic system also works well with the electron-deficient 4-bromophenylboronic acid, providing 85% of 4-bromobenzophenone (Table 1, entry 15). In general, the yield of the carbonylative cross coupling product for substituted boronic acids were lower than the corresponding substituted aryl iodides.

Table 1 Carbonylative Suzuki Coupling Reaction of Aryl Iodides with Various Arylboronic Acids[a]

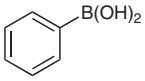
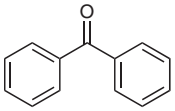
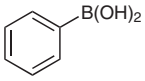
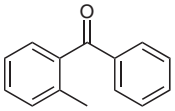
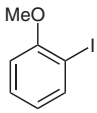
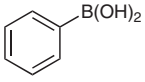
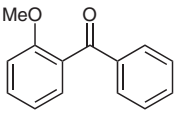
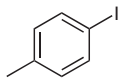
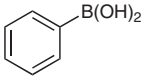
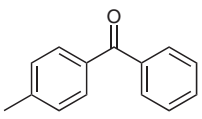
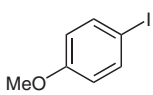
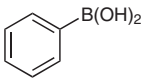
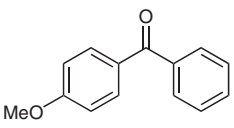
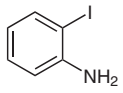
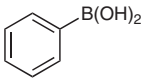
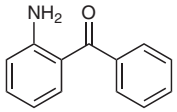
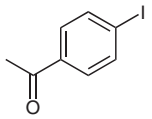
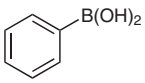
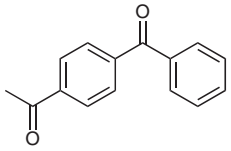
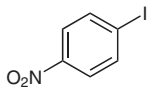
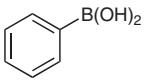
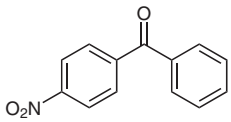
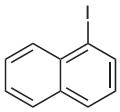
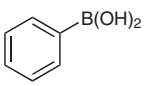
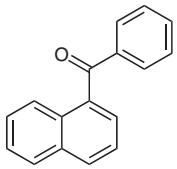
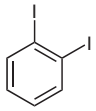
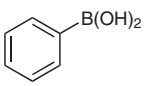
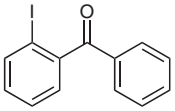
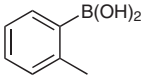
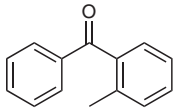
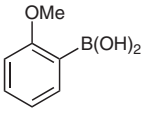
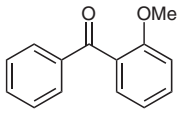
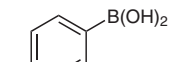
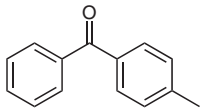
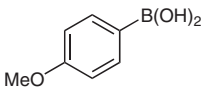
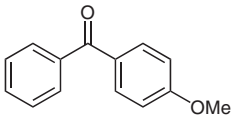
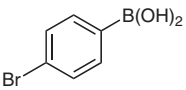
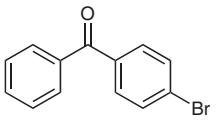
Entry	Aryl iodide	Boronic acid	Product	Yield (%)[b]
1				94
2				90
3				88
4				90
5				91

Table 1 Carbonylative Suzuki Coupling Reaction of Aryl Iodides with Various Arylboronic Acids[a] (continued)

Entry	Aryl iodide	Boronic acid	Product	Yield (%)[b]
6				93
7				95
8				91
9				89
10				31
11				80
12				79
13				82
14				88
15				85

[a] Reaction conditions: aryl iodide (1 mmol), arylboronic acid (1.2 mmol), PS-Pd-NHC (14.5 μmol), K_2CO_3 (3 mmol), toluene (10 mL), 100 °C, CO (100 psi), 10 h.
[b] Isolated yield.

Moreover, the generality of our catalytic system (PS-Pd-NHC) was explored by coupling different arylboronic acids with heteroaryl iodides such as 2-iodopyridine, 3-iodopyridine, 2-iodothiophene, 5-iodoindole, and 3-iodoquinoline in toluene as a solvent and 200 psi CO pressure. The carbonylative Suzuki coupling reaction of 2-iodopyridine and 3-iodopyridine with phenylboronic acid using PS-Pd-NHC complex as a catalyst provides 89% and 91% yield, respectively, of the desired products (Table 2, entries 1, 2). The reaction of sterically hindered electron-rich

arylboronic acids such as 2-methylphenylboronic acid and 2-methoxyphenylboronic acid with 3-iodopyridine offer products in admirable yields (90–93%,Table 2, entries 3, 4). However, 4-bromophenylboronic acid gave moderate yield of the product with 3-iodopyridine (Table 2, entry 5). The reaction of 2-iodothiophene with 2-methylphenylboronic acid, 2-methoxyphenylboronic acid and 3-methylphenylboronic acid provided respective diaryl ketones in 82, 68, and 98% yield, respectively (Table 2, entry 6–8).

Table 2 Carbonylative Suzuki Coupling Reaction of Hetetoaryl Iodides with Various Arylboronic Acids[a]

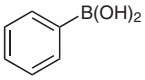
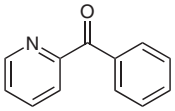
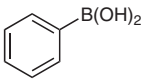
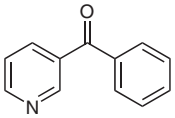
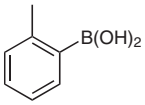
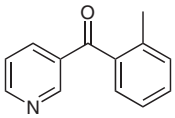
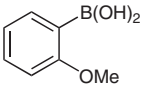
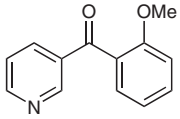
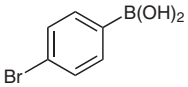
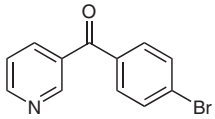
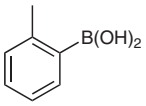
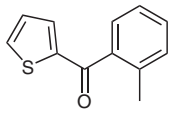
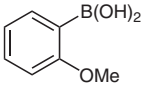
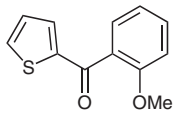
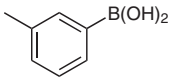
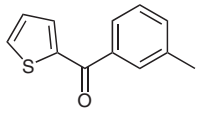
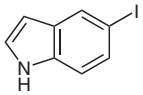
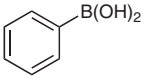
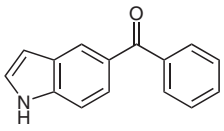
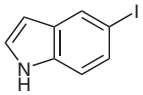
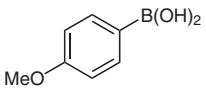
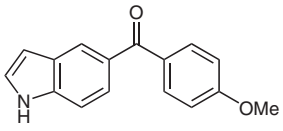
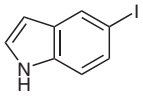
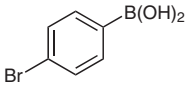
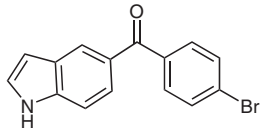
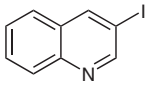
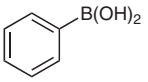
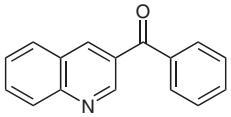
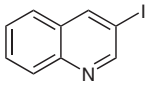
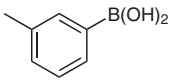
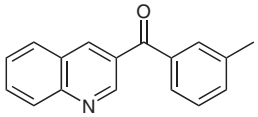
Entry	Aryl iodide	Boronic acid	Product	Yield (%)[b]
1				89
2				91
3				90
4				93
5				70
6				82
7				68
8				98
9				93
10				94
11				90

Table 2 Carbonylative Suzuki Coupling Reaction of Hetetoaryl Iodides with Various Arylboronic Acids[a] (continued)

Entry	Aryl iodide	Boronic acid	Product	Yield (%)[b]
12				95
13				98

[a] Reaction conditions: aryl iodide (1 mmol), arylboronic acid (1.2 mmol), PS-Pd-NHC (14.5 μmol), K_2CO_3 (3 mmol), toluene (10 mL), 100 °C, CO (100 psi), 10 h.
[b] Isolated yield.

Encouraged with these results, the PS-Pd-NHC complex was then subjected for carbonylative Suzuki coupling reactions of 5-iodoindole and 3-iodoquinoline with various arylboronic acids. To the best of our knowledge, there is no general method reported for the synthesis of sterically hindered heteroaryl ketones from iodoindole and iodoquinoline through carbonylative Suzuki cross coupling reaction. It was noticed that 5-iodoindole smoothly undergoes carbonylative coupling reaction with phenylboronic acid, providing 93% yield of heterobiaryl ketone (Table 2, entry 9). Electron-donating and electron-withdrawing groups such as OMe and Br on phenylboronic acid were well tolerated to give the desired biaryl ketone in good to excellent yields (Table 2, entries 10, 11). The reaction of 3-iodoquinoline with phenylboronic acid, provides the desired carbonylative Suzuki coupling product in 95% yield (Table 2, entry 12). Reaction of 3-methylphenylboronic acid with 3-iodoquinoline underwent smoothly with excellent yield of quinolin-3-yl-*m*-tolylmethanone (Table 2, entry 13).

In order to determine whether the catalysis was due to the PS-Pd-NHC complex or due to a homogeneous palladium complex that comes off the support during the reaction and returns back to the support at the end, we performed a hot filtration test.[15] The carbonylative cross coupling reaction of iodobenzene with phenylboronic acid was carried out at 100 °C. Then PS-Pd-NHC complex was filtered off after two hours of reaction time and the filtrate was allowed to react further. The catalyst filtration was performed at 100 °C in order to avoid possible recoordination of soluble palladium upon cooling. We found that, after this hot filtration, no further reaction occurred. This experimental finding suggests that the palladium metal did not leach out of complex at elevated temperature during the progress of reaction. In addition, to reconfirm this observation ICP-AES analysis of the reaction mixture was carried out after 2 hours and after 10 hours, which revealed below detectable level (below 0.01 ppm) of palladium in solution.

To make the synthetic protocol more economical, it is necessary to study the recyclability of PS-Pd-NHC complex. The PS-Pd-NHC catalyst was found to be recycled for consecutive four cycles with maintenance of high activity and selectivity (Table 3). No significant decrease in yield during the three recycles was observed; however, yield declined up to 86% for the fourth cycle. This decrease in yield might be due to handling loss of complex during the study.

Table 3 Recyclability Study of PS-Pd-NHC Complex Catalyst[a]

Entry	PS-Pd-NHC catalyst	Yield (%)[b]
1	fresh	94
2	recycle 1	94
3	recycle 2	93
4	recycle 3	92
5	recycle 4	86

[a] Reaction conditions: iodobenzene (1 mmol), phenylboronic acid (1.2 mmol), PS-Pd-NHC (50 mg, 14.5 μmol), K_2CO_3 (3 mmol), toluene (10 mL), 100 °C, CO (100 psi), 10 h.
[b] GC yield.

In conclusion, an efficient phosphine-free protocol for the carbonylative Suzuki coupling reaction of aryl and heteroaryl iodides using PS-Pd-NHC complex as a heterogeneous and recyclable catalyst has been developed. The reaction was optimized with respect to various parameters and enabled carbonylative Suzuki coupling reaction of different aryl and heteroaryl iodides with variety of arylboronic acids affording good to excellent yield of desired products thus illustrating broad application of the methodology. Further, the PS-Pd-NHC complex was recycled for consecutive four cycles without any significant loss in catalytic activity.

All chemicals and reagents were procured from commercial suppliers and used without further purification. The products were characterized using ^{1}H NMR, ^{13}C NMR spectra (Varian Mercury 300 NMR Spectrometer) and IR (Perkin-Elmer FT-IR) spectroscopic techniques. The reactions progress was monitored via GC (Perkin-Elmer, Clarus 400) (BP-10 GC column, 30 m × 0.32 mm ID, film thickness 0.25 μm). Products were confirmed by GC-MS (Shimadzu GC-MS QP 2010). Polymer-supported Pd-N-hetero-

cyclic carbene complex (PS-Pd-NHC) used was prepared according to the procedure reported in the literature.[13a] Elemental analysis confirms that about 0.29 mmol/g of Pd catalyst was loaded on (chloromethyl)polystyrene resin support. Petroleum ether (PE) used refers to the fraction boiling in the range 60–80 °C.

Carbonylative Suzuki Coupling Reaction of Aryl Iodides with Arylboronic Acid; General Procedure

To a 100 mL autoclave were added aryl iodide (1.0 mmol), arylboronic acid (1.2 mmol), PS-Pd-NHC (50 mg, 14.5 μmol), toluene (10 mL), and K_2CO_3 (415 mg, 3.0 mmol). The mixture was first stirred for 10 min and then flushed with CO, then filled with 100 psi of CO, and the reaction mixture was heated at 100 °C for 10 h. After completion of the reaction, the mixture was cooled to r.t. The catalyst was filtered off and the solvent was removed under reduced pressure. The residue obtained was purified by column chromatography (silica gel, 60–120 mesh; PE–EtOAc, 90:10) to afford the desired carbonylated product (Table 1). The structures of the products were confirmed by GC-MS, ^{1}H NMR, ^{13}C NMR, and IR spectroscopic techniques. The purity of compounds was determined by GC-MS analysis.

Carbonylative Suzuki Coupling Reaction of Heteroaryl Iodides with Arylboronic Acid; General Procedure

To a 100 mL autoclave were added heteroaryl iodide (1.0 mmol), arylboronic acid (1.2 mmol), PS-Pd-NHC (50 mg, 14.5 μmol), toluene (10 mL), and K_2CO_3 (415 mg, 3.0 mmol). The reaction mixture was first stirred for 10 min and then flushed with CO, then filled with 200 psi of CO and the mixture was heated at 100 °C for 10–15 h. After completion of the reaction, the mixture was cooled to r.t. The catalyst was filtered off and the solvent was removed under reduced pressure. The residue obtained was purified by column chromatography (silica gel, 60–120 mesh; PE–EtOAc, 90:10) to afford the desired carbonylated product (Table 2). The structure of the products were confirmed by GC-MS, ^{1}H NMR, ^{13}C NMR, and IR spectroscopic techniques. The purity of compounds was determined by GC-MS analysis.

Recycling of PS-Pd-NHC Complex for Carbonylative Suzuki Coupling Reaction of Iodobenzene with Phenylboronic Acid

After completion of reaction, the reaction mixture was cooled to r.t., and the catalyst was collected by filtration. The filtered catalyst was washed vigorously with distilled H_2O (5 × 10 mL), MeOH (5 × 10 mL), and dried under reduced pressure. The dried catalyst was then used for catalyst recyclability experiment. It was observed that the recovered catalyst could be reused for four consecutive cycles for the carbonylative Suzuki coupling reaction of iodobenzene with phenylboronic acid (94%, 94%, 93%, 92%, 86%, respectively).

Characterization of Selected Compounds

2-Aminobenzphenone (Table 1, entry 6)

Yield: 183 mg (93%); solid.

IR (KBr): 3436, 3318, 3054, 2934, 1626, 1589, 1553, 1479, 1449, 1328, 1303, 1250, 1151, 1025, 938, 912, 745, 703, 645 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.1 (br, 2 H), 6.61–6.55 (t, *J* = 7.9 Hz, 1 H), 6.73–6.70 (d, *J* = 8 Hz, 1 H), 7.3–7.24 (m, 2 H), 7.46–7.42 (t, *J* = 5.9 Hz, 1 H), 7.51–7.49 (d, *J* = 7.3 Hz, 2 H), 7.64–7.61 (d, *J* = 8.1 Hz, 2 H).

^{13}C NMR (75.43 MHz, $CDCl_3$): δ = 199.1 (C=O) 151.0 (C), 140.2 (C), 134.6 (CH), 134.2 (CH), 131.0 (CH), 129.1 (2 CH), 128.1 (2 CH), 118.0 (CH), 117.0 (CH), 115.5 (CH).

MS (EI, 70 eV): *m*/*z* (%) = 197 (100), 120 (41), 105 (16), 92 (31), 77 (44), 65 (36), 51 (19).

4-Acetylbenzophenone (Table 1, entry 7)

Yield: 212 mg (95%); solid.

IR (KBr): 2920, 2852, 1689, 1657, 1593, 1445, 1402, 1358, 1277, 1072, 963, 931, 845, 795, 698 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.66 (s, 3 H), 7.52–7.47 (t, *J* = 7.5 Hz, 1 H), 7.65–7.59 (t, *J* = 8.8 Hz, 1 H), 7.82–7.79 (d, *J* = 8.4 Hz, 2 H), 7.88–7.87 (d, *J* = 8.4 Hz, 2 H), 8.07–8.04 (d, *J* = 8.8 Hz, 2 H).

^{13}C NMR (75.43 MHz, $CDCl_3$): δ = 197.5 (C=O), 195.9 (C=O), 141.4 (C), 139.6 (C), 137.0 (C), 133.0 (CH), 130.11 (2 CH), 130.05 (2 CH), 128.5 (2 CH), 128.2 (2 CH), 22.7 (CH_3).

MS (EI, 70 eV): *m*/*z* (%) = 224 (53), 209 (100), 181 (10), 147 (35), 105 (80), 77 (78), 43 (35).

2-Iodobenzophenone (Table 1, entry 10)

Yield: 95 mg (31%); solid.

IR (KBr): 3059, 2922, 2852, 1743, 1669, 1595, 1580, 1448, 1314, 1285, 1251, 1194, 1157, 1078, 1015, 927, 799, 762, 703, 954 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.31–7.17 (m, 1 H), 7.50–7.41 (m, 3 H), 7.62–7.55 (m, 2 H), 7.81–7.78 (d, *J* = 8.4 Hz, 1 H), 7.93–7.9 (d, *J* = 8.1 Hz, 2 H).

^{13}C NMR (75.43 MHz, $CDCl_3$): δ = 197.2 (C=O), 144.7 (C), 139.8 (C), 135.7 (CH), 133.7 (CH), 132.4 (CH), 131.2 (CH), 130.5 (2 CH), 128.7 (2 CH), 127.8 (CH), 92.3 (C).

MS (EI, 70 eV): *m*/*z* (%) = 308 (10), 231 (28), 203 (10), 181 (18), 152 (23), 105 (100), 77 (76), 45 (71).

Pyridin-3-yl-*o*-tolylmethanone (Table 2, entry 3)

Yield: 177 mg (90%); solid.

IR (KBr): 2925, 2851, 1729, 1670, 1584, 1463, 1292, 1270, 1190, 1081, 1025, 966, 925, 796, 737, 650 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.38 (s, 3 H), 7.46–7.26 (m, 5 H), 8.16–8.14 (d, *J* = 8.1 Hz, 1 H), 8.81–8.79 (d, *J* = 6.2 Hz, 1 H), 8.93 (s, 1 H).

^{13}C NMR (75.43 MHz, $CDCl_3$): δ = 196.8 (C=O), 153.1 (CH), 151.3 (CH), 147.1 (C), 137.3 (CH), 133.4 (C), 131.5 (C), 131.1 (CH), 129.0 (CH), 125.5 (CH), 123.6 (CH), 119.0 (CH), 14.1 (CH_3).

MS (EI, 70 eV): *m*/*z* (%) = 196 (100), 197 (45), 182 (5), 168 (34), 141 (5), 119 (51), 106 (11), 91 (75), 89 (22), 78 (30), 65 (41), 51 (31), 45 (34).

(2-Methoxyphenyl)pyridin-3-ylmethanone (Table 2, entry 4)

Yield: 198 mg (93%); solid.

IR (KBr): 2922, 2852, 1667, 1599, 1487, 1464, 1300, 1246, 1162, 1111, 1023, 927, 827, 756, 713, 648 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.69 (s, 3 H), 7.02–6.99 (d, *J* = 8.4 Hz, 1 H), 7.10–7.05 (dd, *J* = 7.3, 7.69 Hz, 1 H), 7.54–7.38 (m, 3 H), 8.14–8.11 (d, *J* = 8.1 Hz, 1 H), 8.75–8.73 (d, *J* = 6.6 Hz, 1 H), 8.91 (s, 1 H).

^{13}C NMR (75.43 MHz, $CDCl_3$): δ = 194.9 (C=O), 157.5 (C), 152.8 (CH), 151.1 (CH), 136.6 (CH), 133.4 (C), 133.0 (CH), 130.1 (CH), 127.5 (CH), 123.3 (CH), 120.9 (C), 111.4 (CH), 55.4 (CH_3).

MS (EI, 70 eV): *m*/*z* (%) = 213 (30), 182 (4), 135 (100), 107 (11), 92 (25), 77 (51), 64 (11), 51 (32), 45 (29).

Thiophen-2-yl-*o*-tolylmethanone (Table 2, entry 6)

Yield: 165 mg (82%); solid.

IR (KBr): 3449, 2962, 1641, 1513, 1411, 1354, 1297, 1262, 1097, 1047, 848, 795, 733 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.38 (s, 3 H), 7.12–7.11 (dd, *J* = 3.66, 4.0 Hz, 1 H), 7.30–7.25 (m, 2 H), 7.45–7.36 (m, 2 H), 7.71–7.70 (d, *J* = 1.1 Hz, 1 H), 7.73–7.72 (d, *J* = 1.1 Hz, 1 H).

^{13}C NMR (75.43 MHz, $CDCl_3$): δ = 190.5 (C=O), 145.0 (C), 138.5 (C), 136.5 (C), 135.5 (CH), 134.9 (CH), 131.1 (CH), 130.4 (CH), 128.1 (CH), 125.2 (CH), 14.2 (CH_3).

MS (EI, 70 eV): *m*/*z* (%) = 202 (100), 187 (5), 169 (28), 141 (24), 128 (10), 119 (15), 111 (59), 91 (47), 83 (13), 65 (34), 45 (14).

(2-Methoxyphenyl)thiophen-2-yl-methanone (Table 2, entry 7)
Yield: 148 mg (68%); solid.

IR (KBr): 3359, 2923, 2851, 1644, 1599, 1459, 1411, 1354, 1264, 1163, 1108, 1050, 1023, 884, 844, 757, 643 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.78 (s, 3 H), 6.95–6.92 (d, *J* = 8.4 Hz, 1 H), 7.10–6.98 (m, 2 H), 7.46–7.38 (dd, *J* = 4.4, 7.3 Hz, 1 H), 7.66 (d, *J* = 1.1 Hz, 1 H), 7.85 (d, *J* = 1.83 Hz, 1 H), 7.87 (d, *J* = 1.46 Hz, 1 H).

^{13}C NMR (75.43 MHz, $CDCl_3$): δ = 188.2 (C=O), 164.5 (C), 144.9 (C), 135.2 (CH), 134.6 (CH), 132.9 (CH), 131.9 (CH), 129.2 (CH), 121.2 (CH), 120.2 (C), 111.6 (CH), 55.7 (CH_3).

MS (EI, 70 eV): *m*/*z* (%) = 218 (62), 201 (23), 185 (73), 173 (21), 135 (65), 121 (63), 111 (100), 105 (20), 92 (35), 77 (65), 45 (15).

Thiophen-2-yl-*m*-tolylmethanone (Table 2, entry 8)
Yield: 197 mg (98%); solid.

IR (KBr): 3391, 3100, 2921, 1633, 1513, 1412, 1353, 1289, 1209, 1123, 1052, 931, 861, 776, 735, 652 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.41 (s, 3 H), 7.15–7.14 (dd, *J* = 4.03, 3.66 Hz, 1 H), 7.37–7.32 (m, 2 H), 7.66–7.62 (m, 3 H), 7.70–7.68 (d, *J* = 4.8 Hz, 1 H).

^{13}C NMR (75.43 MHz, $CDCl_3$): δ = 188.4 (C=O), 156.4 (CH), 143.5 (C), 138.2 (CH), 137.9 (CH), 134.9 (C), 134.2 (CH), 133.0 (CH), 129.5 (CH), 128.1 (CH), 126.3 (CH), 21.2 (CH_3).

MS (EI, 70 eV): *m*/*z* (%) = 202 (68), 187 (25), 174 (4), 141 (3), 119 (48), 111 (100), 91 (40), 83 (10), 65 (26), 45 (15).

(1*H*-Indol-5-yl)phenylmethanone (Table 2, entry 9)
Yield: 205 mg (93%); solid.

IR (KBr): 3292, 2923, 2851, 1621, 1607, 1572, 1431, 1322, 1116, 1092, 957, 880, 734 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.62 (d, *J* = 2.2 Hz, 1 H), 7.27–7.26 (dd, *J* = 2.56, 2.93 Hz, 1 H), 7.45–7.44 (m, 3 H), 7.50–7.47 (d, *J* = 8.06 Hz, 1 H), 7.57–7.55 (d, *J* = 7.3 Hz, 1 H), 7.83–7.77 (dd, *J* = 6.96, 8.8 Hz, 2 H), 8.13 (s, 1 H), 8.93 (br, 1 H).

^{13}C NMR (75.43 MHz, $CDCl_3$): δ = 197.0 (C=O), 139.0 (C), 138.5 (C), 131.8 (CH), 123.0 (2 CH), 129.6 (C), 128.2 (2 CH), 127.2 (C), 126.0 (CH), 125.4 (CH), 124.2 (CH), 111.2 (CH), 104.1 (CH).

MS-MS (ESI+): *m*/*z* calcd for (M + 1): 222.08; found (M + 1): 222.1.

(1*H*-Indol-5-yl)(4-methoxyphenyl)methanone (Table 2, entry 10)
Yield: 235 mg (94%); solid.

IR (KBr): 3262, 2929, 2840, 1624, 1508, 1420, 1308, 1252, 1175, 1116, 1093, 1029, 964, 885, 849, 823, 760, 731, 614, 576 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.88 (s, 3 H), 6.60 (d, *J* = 2.2 Hz, 1 H), 6.98–6.95 (d, *J* = 8.8 Hz, 2 H), 7.26–7.25 (d, *J* = 2.6 Hz, 1 H), 7.42–7.40 (d, *J* = 8.4 Hz, 1 H), 7.73–7.70 (d, *J* = 7 Hz, 1 H), 7.86–7.83 (d, *J* = 8.8 Hz, 2 H), 8.10 (s, 1 H), 8.90 (br, 1 H).

^{13}C NMR (75.43 MHz, $CDCl_3$): δ = 196.7 (C=O), 162.8 (C), 138.2 (C), 132.6 (2CH), 131.4 (C), 130.2 (C), 127.2 (C), 125.9 (CH), 124.9 (CH), 124.1 (CH), 113.6 (CH), 113.4 (CH), 111.1 (CH), 104.2 (CH), 55.5 (CH_3).

MS-MS (ESI+): *m*/*z* calcd for (M + 1): 252.09; found (M + 1): 252.1.

(4-Bromophenyl)(1*H*-indol-5-yl)methanone (Table 2, entry 11)
Yield: 270 mg (90%); solid.

IR (KBr): 3269, 1644, 1595, 1429, 1329, 1284, 1203, 1330, 1284, 1203, 1100, 1067, 1011, 977, 878, 841, 773, 754, 729 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.65 (d, *J* = 2.2 Hz, 1 H), 7.30–7.26 (d, *J* = 12.46 Hz, 1 H), 7.47–7.44 (d, *J* = 8.8 Hz, 2 H), 7.70–7.67 (d, *J* = 8.4 Hz, 2 H), 7.77–7.73 (d, *J* = 9.9 Hz, 2 H), 8.09 (s, 1 H), 8.60 (br, 1 H).

^{13}C NMR (75.43 MHz, $CDCl_3$): δ = 196.3 (C=O), 138.5 (C), 137.8 (C), 131.6 (2 CH), 131.5 (2 CH), 129.5 (C), 127.3 (C), 126.6 (C), 125.6 (CH), 125.2 (CH), 124.2 (CH), 111.2 (CH), 104.4 (CH).

MS-MS (ESI+): *m*/*z* calcd for (M + 1): 299.99; found (M + 1): 300.0.

Phenylquinolin-3-yl-methanone (Table 2, entry 12)
Yield: 234 mg (95%); solid.

IR (KBr): 3052, 2924, 2853, 1649, 1598, 1572, 1493, 1445, 1367, 1290, 1245, 1178, 1122, 935, 911, 860, 759, 726, 698, 595 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.55 (m, 3 H), 7.67–7.5 (dd, *J* = 7.7, 8.1 Hz, 1 H), 7.87–7.80 (m, 2 H), 7.92–7.89 (d, *J* = 8.1 Hz, 2 H), 8.20–8.18 (d, *J* = 8.43 Hz, 1 H), 8.53 (s, 1 H), 9.33 (s, 1 H).

^{13}C NMR (75.43 MHz, $CDCl_3$): δ = 194.8 (C=O), 150.3 (CH), 149.4 (C), 138.8 (CH), 137.0 (C), 133.1 (CH), 131.9 (CH), 130.0 (2 CH), 129.4 (C), 129.2 (C), 128.6 (3 CH), 127.6 (CH), 126.6 (CH).

MS (EI, 70 eV): *m*/*z* (%) = 233 (100), 204 (12), 176 (3), 156 (29), 128 (50), 105 (66), 77 (78), 45 (89).

Quinolin-3-yl-*m*-tolylmethanone (Table 2, entry 13)
Yield: 242 mg (98%); solid.

IR (KBr): 3057, 2917, 1656, 1617, 1596, 1495, 1415, 1368, 1292, 1189, 1039, 788, 758, 588 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.42 (s, 3 H), 7.45–7.38 (m, 2 H), 7.67–7.60 (dd, *J* = 7.3, 7.0 Hz, 1 H), 7.95–7.81 (m, 4 H), 8.23–8.20 (d, *J* = 8.8 Hz, 1 H), 8.56 (s, 1 H), 9.31 (s, 1 H),

^{13}C NMR (75.43 MHz, $CDCl_3$): δ = 194.8 (C=O), 149.9 (CH), 148.9 (C), 138.9 (C), 138.7 (CH), 138.4 (CH), 134.6 (C), 133.8 (CH), 131.8 (CH), 130.9 (C), 130.2 (CH), 130.0 (C), 129.1 (CH), 128.3 (CH), 127.5 (CH), 126.5 (CH), 21.1 (CH_3).

MS (EI, 70 eV): *m*/*z* (%) = 247 (100), 232 (81), 218 (7), 204 (6), 156 (30), 128 (57), 119 (78), 101 (40), 91 (75), 75 (19), 65 (34), 51 (14), 45 (27).

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References

(1) *The Merck Index*, 11th ed.; Budavari, S., Ed.; Merck: Rahway, **1989**.
(2) (a) Fürstner, A.; Voigtländer, D.; Schrader, W.; Giebel, D.; Reetz, M. T. *Org. Lett.* **2001**, *3*, 417. (b) Song, C. E.; Shim, W. H.; Roh, E. J.; Choi, J. H. *Chem. Commun.* **2000**, 1695. (c) Fillion, E.; Fishlock, D.; Wilsily, A.; Goll, J. M. *J. Org. Chem.* **2005**, *70*, 1316.

(3) (a) Bonnaire, S.; Carpentier, J. F.; Mortreux, A.; Castanet, Y. *Tetrahedron Lett.* **2001**, *42*, 3689. (b) Bonnaire, S.; Carpentier, J. F.; Mortreux, A.; Castanet, Y. *Tetrahedron* **2003**, *59*, 2793.
(4) Ishiyama, T.; Kizaki, H.; Hayashi, T.; Suzuki, A.; Miyaura, N. *J. Org. Chem.* **1998**, *63*, 4726.
(5) Maerten, E.; Hassouna, F.; Bonnaire, S.; Mortreux, A.; Carpentier, J. F.; Castanet, Y. *Synlett* **2003**, 1874.
(6) Andrus, M. B.; Ma, Y.; Zang, Y.; Song, C. *Tetrahedron Lett.* **2002**, *43*, 9137.
(7) Cai, M.; Zheng, G.; Zha, L.; Peng, J. *Eur. J. Org. Chem.* **2009**, 1585.
(8) Mingji, D.; Liang, B.; Wang, C.; You, Z.; Xiang, J.; Dong, G.; Chen, J.; Yang, Z. *Adv. Synth. Catal.* **2004**, *346*, 1669.
(9) Neumann, H.; Brennfhrer, A.; Beller, M. *Adv. Synth. Catal.* **2008**, *350*, 2437.
(10) Petz, A.; Peczely, G.; Pinter, Z.; Kollar, L. *J. Mol. Catal. A: Chem.* **2006**, *255*, 97.
(11) (a) Ofele, K. *J. Organomet. Chem.* **1968**, *12*, 42. (b) Wanzlick, H. J.; Schönherr, H. J. *Angew. Chem. Int. Ed.* **1968**, *7*, 141. (c) Herrmann, W. A. *Angew. Chem. Int. Ed.* **2002**, *41*, 1290.
(12) (a) Weskamp, T.; Kohl, F. J.; Hieringer, W.; Gleich, D.; Herrmann, W. A. *Angew. Chem. Int. Ed.* **1999**, *38*, 2416. (b) Schwarz, J.; Biihm, V. P. W.; Gardiner, M. G.; Grosche, M.; Herrmann, W. A.; Hieringer, W.; Raudaschl-Sieber, G. *Chem. Eur. J.* **2000**, *6*, 1773.
(13) (a) Byun, J. W.; Lee, Y. S. *Tetrahedron Lett.* **2004**, *45*, 1837. (b) Kim, J. W.; Kim, J. H.; Lee, D. H.; Lee, Y. S. *Tetrahedron Lett.* **2006**, *47*, 4745. (c) Tandukar, S.; Sen, A. *J. Mol. Catal., A: Chem.* **2007**, *268*, 112. (d) Gomann, A.; Deverell, J. A.; Munting, K. F.; Jones, R. C.; Rodemann, T.; Canty, A. J.; Smith, J. A.; Guijt, R. M. *Tetrahedron* **2009**, *65*, 1450.
(14) (a) Tambade, P. J.; Patil, Y. P.; Bhanage, B. M. *Appl. Organomet. Chem.* **2009**, *23*, 235. (b) Tambade, P. J.; Patil, Y. P.; Bhanushali, M. J.; Bhanage, B. M. *Synthesis* **2008**, 2347. (c) Tambade, P. J.; Patil, Y. P.; Bhanushali, M. J.; Bhanage, B. M. *Tetrahedron Lett.* **2008**, *49*, 2221. (d) Tambade, P. J.; Patil, Y. P.; Panda, A. G.; Bhanage, B. M. *Eur. J. Org. Chem.* **2009**, 3022.
(15) (a) Lempers, H. E. B.; Sheldon, R. A. *J. Catal.* **1998**, *175*, 62. (b) Zhao, H.; Zheng, G.; Sheng, S.; Cai, M. *Catal. Commun.* **2009**, *11*, 158.